

WASTEWATER CONTAMINANTS MEASURED TO SUPPORT THE NEW JERSEY TOXICS REDUCTION PROGRAM – PART 2: DIOXIN, PCB, AND ORGANOCHLORINE PESTICIDE PROFILES

Mary Schrock¹, Karen Tracy¹, Mark Misita¹, Joseph Tabor¹, Gregory Durell², Deirdre Dahlen², Bo Liu², Mick DeGraeve³, and Dennis McCauley³

1 Battelle Memorial Institute, 505 King Ave., Columbus, OH 43201, USA

2 Battelle Memorial Institute, 397 Washington Street, Duxbury, MA 02332, USA

3 Great Lakes Environmental Center, 739 Hastings St., Traverse City, MI 49684, USA

Introduction

The New Jersey Toxics Reduction Program (NJ-TRP) aims to increase understanding of the importance of point and non-point contaminant sources to the New York-New Jersey (NY-NJ) Harbor. Twelve publicly owned treatment works (POTW) in NJ discharge roughly 30% of the total wastewater from treatment facilities in NY and NJ to the Harbor. These POTWs serve residential, commercial, and industrial operations. Combined sewer and storm water outfalls (CSO/SWO) contribute untreated flows to the Harbor during storms, and their large volume discharges may make these significant contaminant sources. Additional information on the NJ-TRP and results for PAH in wastewater discharges are described elsewhere.¹ For this paper, analytical methods for PCDD/PCDF, PCBs, and organochlorine pesticides modified to improve sensitivity for measuring low concentration contaminants are discussed. Concentrations of these analytes in samples from four POTW sampling events and two CSO/SWO storm sampling events from 2000 to 2002 are presented.

Methods and Materials

Composite samples (20L) of effluent were split in the field to create individual 2.5 L samples for each analysis. The samples were pressure filtered, and the filter and filtrate were spiked with labeled internal standards. Filters were Soxhlet extracted with toluene for PCDD/PCDF, methylene chloride (DCM) for PCB, and 50% acetone/50% DCM for pesticides. Filtrates were liquid-liquid extracted with DCM followed by 80% DCM/20% acetone for all analytes. For the first POTW sampling event, the filters and filtrates were prepared as separate samples to evaluate the distribution of analytes between dissolved and particulate phases. For the remaining POTW sampling events and each of the CSO/SWO sampling events, 75% of each filter and corresponding filtrate extract were combined for cleanup and analysis; the remaining 25% was archived. Extracts were cleaned and analyzed for PCDD/PCDF, individual PCB congeners, and 28 pesticides following general procedures described in U.S. EPA Method 1613, Revision B²; U.S. EPA Method 1668, Revision A³, and modified NYSDEC Method HRMS-2⁴, respectively. Methods are detailed in the project's Final Quality Assurance Project Plan⁵. Table 1 shows the concentration factors achieved and detection limits obtained using these analytical procedures.

Table 1. Sample Processing Factors

Analyte	Sample Volume (L)	Final Extract Volume (μL)	Concentration Factor	Low Calibration Conc. (pg/μL)	Detection Limit * (pg/L)
PCDD/PCDF	2.5	20	125,000	0.25 – 2.5	2.7 – 27
PCB	2.5	50	50,000	0.2	5.3
Pesticides	2.5	200	12,500	2.5	266

* Detection limit adjusted for the 75/25 % sample split.

Results and Discussion

PCDD/PCDF data, expressed in terms of tetra-dioxin toxicity equivalents (TEQ)⁶, are shown in Figures 1 and 2. PCDD/PCDF concentrations in the POTW samples were less than 2 pg TEQ/L. While the two highest TEQ samples are from POTWs receiving considerable industrial input, the TEQ values are so low overall that significant differences between partially industrial and primarily sanitary POTWs is difficult to discern. POTW samples were dominated by hepta- and octa-chlorinated congeners; however, these congeners contributed relatively little to the TEQ because of their low toxicity equivalency factors (TEF). Almost every 2,3,7,8-PCDD/PCDF congener was present in all CSO/SWO samples. PCDD/PCDF concentrations ranged from 1.7 to 146 pg TEQ/L, with most of the sites contributing 4 to 40 pg TEQ/L. Separate filter and filtrate results from POTW sampling Event 1 showed that PCDD/PCDF were strongly associated with the particulate phase.

Total PCB concentrations, shown in Figures 3 and 4, were reasonably similar between both types of POTW samples and CSO/SWO samples, with the majority having total PCB concentrations of 50 ng/L or less. Figure 5 shows the typical distribution of PCBs by chlorination level for both the POTW and CSO/SWO samples. With the exception of POTW site 9, both the POTW and CSO samples show increasing concentrations of PCBs from mono- to penta- chlorination with subsequent decreasing concentrations from penta- to deca- chlorination. Approximately half of the PCB detected at POTW Site 9 was from a single di-chlorinated congener, PCB 11. This has been identified as a by-product of a specific industrial pigment manufacturing process. POTW sampling Event 1 filter and filtrate results showed that the PCBs were almost evenly distributed between the two phases; slightly more was associated with the particulate phase than the dissolved phase.

Total pesticide results are shown in Figures 6 and 7. As with the PCBs, the pesticides are present in POTW and CSO/SWO samples at similar concentrations (less than 50 ng/L) for all but a few CSO/SWO sites. Table 2 compares the most abundant pesticides and their percent contribution to the total pesticide concentration for the two types of POTW samples and for the CSO/SWO samples. Gamma-BHC and chlordane were often predominant in partially industrial POTW samples, while a greater variety of pesticides contributed to the pesticide loadings from primarily sanitary POTWs and CSO/SWOs. Separate filter and filtrate results for POTW sampling Event 1 showed that of the predominant pesticides, gamma-BHC was largely associated with the dissolved phase, dieldrin and methoxychlor were more evenly split between the dissolved phase and particulates, and the remaining pesticides were more closely associated with particulates.

The data generated in this project along with other data collection efforts will support the NJ-TRP management actions and improve the understanding of the relative importance of point and non-point sources of contaminants to the NY-NJ Harbor.

Acknowledgments

The authors wish to thank Bridget McKenna and Patty Lopes (Passaic Valley Sewerage Commissioners) for assistance with sample collection and Battelle's high resolution mass spectrometry sample preparation staff for sample extraction and cleanup.

Table 2. Percent Contribution to Total Pesticide Concentration

	POTW- Partially Industrial (%)	POTW-Primarily Sanitary (%)	CSO/SWO (%)
Gamma-BHC	<10-60	<10-29	<10
cis- + trans-chlordane	<10-46	<10-36	<10-39
dieldrin	<10-12	<10-14	<10-36
transnonachlor	<10-20	<10-22	<10-19
4,4'-DDT	<10	<10-20	<10-25
4,4'-DDE	<10	<10-17	<10-13
methoxychlor	<10	<10-48	<10-12
2,4'-DDD	<10	<10-20	<10
4,4'-DDD	<10	<10	<10-23

References

- Liu B., Durell G., Dahlen D., Schrock M., DeGraeve M. and McCauley D. (2003) Wastewater Contaminants Measured To Support The New Jersey Toxics Reduction Program – Part 1: Program Overview And PAH Profiles, Organohalogen Compounds (submitted).
- U.S. EPA Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B (1994), EPA 821-B94-0059. Office of Water, Engineering and Analysis Division.
- U.S. EPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS (1999), EPA 821-R-00-002. Office of Water, Engineering and Analysis Division.
- NY State Department of Environmental Conservation. (1998) Analytical Procedures for Organochlorine Pesticides by Isotope Dilution HRGC/HRMS NYSDEC Method HRMS-2.
- Battelle. (2000) Final Quality Assurance Project Plan, Version 1, Analytical Support for the New Jersey Toxics Reduction Program.
- van den Berg M., Birnbaum L., Bosveld ATC, et al. (1998) Toxicity Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife, Environ Health Perspect 106 (12): 775-792.



